Temperature Dependent Performance of $Li_xM_{y-2}O_4$: *In situ* XRD and XAS Studies

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Abstract No. uria6508
Beamline(s): **X18A, X18B**

Introduction: Spinel $LiMn_2O_4$ based cathode materials are attractive for rechargeable Li-ion batteries, being environmentally benign, cheap, and easy to synthesize. However, the cycling behavior and capacity is intimately related to composition (Li rich, cation deficient or doped with other transition elements such as Ni). Besides the composition, being a mixed valent Mn system with Jahn Teller active Mn^{3+} sites, the temperature plays a role in the phase transformations with cooperative Jahn Teller distortions at just below room temperature (280K). This was first reported by Yamada[i] who showed a transformation from a pure cubic phase to a mixed phase of cubic and tetragonal distortions. Rousse[ii] later reported a pure cubic to orthorhombic transition with a super lattice structure. Charge ordering of Mn^{3+}/Mn^{4+} was reported by Rodriguez[iii] et. al., for the observed orthorhombic phase with lattice super structure. Li rich and doped materials have shown to be resistant to structural change but not under prolong cycling at low temperatures.[iv, v]

This investigation intends to examine $LiMn_2O_4$ compositions (Li rich and doped) cycled at low temperatures over prolong periods of time. The objective is to identify new materials and synthesis routes that result in cathodic materials that are resistant to structural changes and reduced capacity during low temperature operations over a prolonged number of cycles and different charge/discharge rates.

Results/Conclusions: For Li rich materials ($Li_{1+x}Mn_2O_4$), we have found that the structural changes and decrease in the material's capacity occurs over the course of several cycles. A cubic to orthorhombic transformation was observed prior to cycling at 263 K. The time frame of this transition occurred over several hours. When cycling of the material began, the orthorhombic phase was lost and at the end of one cycle the discharge state structure was a mixture of cubic and tetragonal phase. Our initial results have shown that Li rich materials with $x = 1.03 \rightarrow 1.06$ as reported by commercial vendors do not show any initial signs of phase transformations. But over the period of several cycles (12 charge/discharge cycles at C/10 rate), the differential capacitance profile shows the beginnings of phase transformations and the mechanism by which the Li ions move in and out of the cathode material.

The structural transformations that we observed at low temperatures which can also be induced by the intercalation of excess Li by taking the electrochemical cell below 3.3 V is fully reversible. *In situ* XRD and XAS of $LiM_yMn_{2-y}O_4$ materials made via different synthesis routes, cycled at low temperatures are currently in progress at the NSLS.

Acknowledgments: The authors wish to acknowledge the financial support from Northeastern University (start up grant) and the U. S. Department of Energy (Cooperative Research and Development Agreement, CRADA). The authors also gratefully acknowledge the financial support from the U.S. Department of Energy, Division of Materials Science for its role in the development and operation of beam line X11A at the NSLS under contract number DE-FG05-89ER45384. The NSLS is supported by the Department of Energy, Division of Material Science under contract number DE-AC02-98CH 10886.

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